3 2.2. Interaction of one electron atoms with static external electric and magnetic fields

Useful for: Probing; trapping and controlling atoms
Probing fields

2.2.1. The Stark effect, electric fields

Hamiltonian for electron in both: ~~combined~~ electric fields of core and external field:

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{(4\pi\varepsilon_0)r}}_{\hat{H}_0} + \underbrace{e\vec{E}\cdot\vec{r}}_{\hat{H}'} \qquad (2.10)$$

- Let us assume $\vec{E} = E_0 \hat{k}$ (along z-axis) and constant across atom
- Hamiltonian (2.10) assumes $\vec{E}$-field strong enough for fine-structure to be negligible
- S.Equation can still be solved analytically (parabolic coordinates), see book.
- Here, perturbation theory: $\hat{H}_0 + \hat{H}'$

Linear Stark effect:

First order energy shift of state $|nlm\rangle$ from Eq. (1.26)

$$\Delta E = e\vec{E}\cdot\underbrace{\langle\phi_{nlm}|\vec{r}|\phi_{nlm}\rangle}_{=0\ \forall\ nlm \text{ (assignment 1)}} = 0 \qquad (2.11)$$

But careful ⚠, we cannot apply (1.26) if states are degenerate. So first order shift $\Delta E = 0$ for $|100\rangle$ only.

For others need Eq. (1.28), degenerate perturbation theory

So fix $n = n_0$ and write $\underbrace{\langle\phi_{n_0 lm}|e\vec{E}\cdot\vec{r}|\phi_{n_0 l'm'}\rangle}_{=\underline{H'}}$ as a matrix e.g. for $n_0=2$ Eq. (1.28) becomes

$$\begin{bmatrix} 0 & 0 & H'_{00} & 0 \\ 0 & & & \\ H'_{00} & & 0 & \\ 0 & & & \end{bmatrix} \begin{bmatrix} c_{200} \\ c_{21-1} \\ c_{210} \\ c_{211} \end{bmatrix} = E^{(1)}_{n=2} \begin{bmatrix} c_{200} \\ c_{21-1} \\ c_{210} \\ c_{211} \end{bmatrix} \qquad (2.12)$$

(see also later chapter 3, dipole selection rules)

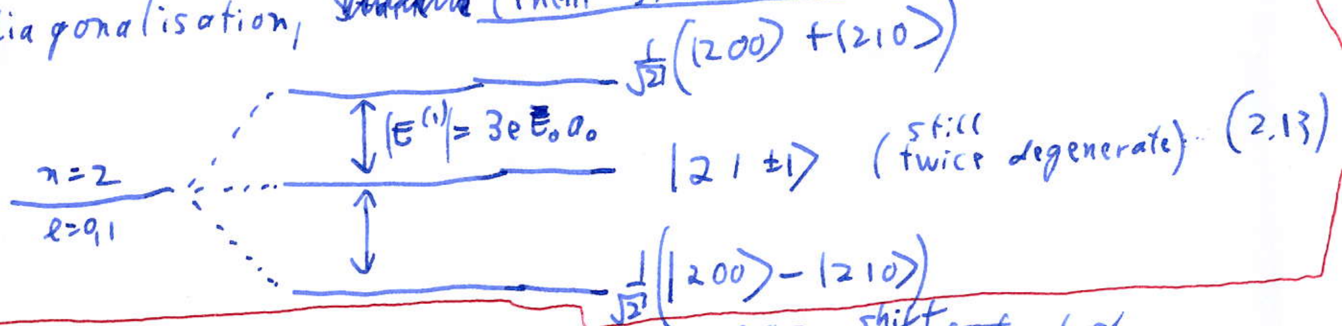
First:

- Used $eE_0\langle \phi_{n_0} l m | r\cos\theta | \phi_{n_0} l' m'\rangle \sim \delta_{l l'\pm1}\,\delta_{mm'}$

  explicit integration / or $\hat{A}'$ odd under parity; $[\hat{H}'_1, \hat{L}_z] = 0$

- $H'_{00} = eE_0\langle\phi_{200}|r\cos\theta|\phi_{210}\rangle = -3ea_0E_0$ (do explicitly like for assignment)

- After diagonalisation, (linear Stark effect)



(2.13)

- So there is a first order (linear) shift for degenerate states.

Non-linear Stark effect

For non-degenerate states (here $|100\rangle$), go to second order PT:

$$\Delta E^{(2)}_{100} = \sum_{\substack{n\neq1\\ l,m}} \frac{|\langle\phi_{nlm}|eE_0 z|100\rangle|^2}{E_{100}-E_{nlm}} \qquad (2.14)$$

- As above, all matrix elements $|\langle\phi_{n10}|eE_0z|100\rangle|^2$ will be non-zero. $E_{100}-E_{n10} < 0$
- (*) includes continuum (unbound states)

$\Delta E^{(2)}_{100} < 0$ and $\sim (eE_0)^2 \Rightarrow$ quadratic stark effect

Interpretation: Non-degenerate states have no permanent dipole moment. However the external field can induce one $\sim E$, which then in turn interacts with the field $\sim E^2$
→ see assignment!

2.22 The Zeeman effect, magnetic fields

Hamiltonian for electron in electric field of core and external magnetic field:

added as in 2.1.2.

$$\hat{H} = \underbrace{\frac{1}{2m}\left(\hat{p} + e\vec{A}\right)^2 - \frac{Ze^2}{(4\pi\varepsilon_0)r}}_{\text{see eq. n}} \overbrace{+ \frac{g_s\mu_B}{\hbar}\vec{B}\cdot\hat{S}_z + \xi(r)\vec{L}\cdot\vec{S}} \quad (2.15)$$

$\bar{e}$ spin, see Eq. (2.2)

classical vector-potential:

$$\vec{A} = \frac{1}{2}\left(\vec{B}\times\vec{r}\right) \quad \text{for constant } B\text{-field} \quad (2.16)$$

Insert $\vec{A}, \hat{p}$ & lots of vector calculus (see book)

see Eq. (2.2)

$$\hat{H} = \Big[\underbrace{-\frac{\hbar^2}{2m}\nabla^2}_{\hat{H}a} \underbrace{- \frac{Ze^2}{(4\pi\varepsilon_0)r}}_{\hat{H}b} \underbrace{+ \xi(r)\vec{L}\cdot\vec{S}}_{\hat{H}c} \underbrace{+ \frac{\mu_B}{\hbar}\left(\vec{L}+2\vec{S}\right)\vec{B}}_{\hat{H}d} \underbrace{+\frac{e^2}{8m}\left(\vec{B}\times\vec{r}\right)^2}_{\hat{H}e}\Big] \quad (2.17)$$

see Eq. (2.1)

let $\vec{B} = B_0\hat{k}$ (along z-axis)

Now analyze Eq. (2.17) with PT depending on relative importance of terms a–e, which depends on $|\phi_{n\ell m}\rangle$ and $|\vec{B}|$

Linear Zeeman effect (strong B-field)

- Energy due to magnetic field large compared to finestructure.

$\hat{H}_0 = \hat{H}_a + \hat{H}_b + \hat{H}_d$ first neglect $\hat{H}_c, \hat{H}_e$

$$\hat{H}_d = \frac{\mu_B}{\hbar}B_0\left(\hat{L}_z + 2\hat{S}_z\right)$$

So $|\phi_{n\ell m}\rangle|\chi\rangle$ of Eq. (1.166) are already eigenfunctions of $\hat{H}$ in Eq. (2.17), solving

$$\hat{H}_0|\phi_{n\ell m s}\rangle = E_{n\ell s}|\phi_{n\ell m s}\rangle$$

for Zeeman-shifted energies

$$\boxed{E_{n\ell s} = E_n + \mu_B B_0\left(m_\ell + 2m_s\right) \quad m_s = \pm\frac{1}{2} \quad (2.18)}$$

see Eq. (1.19)

- interpretation: $\vec{L}, \vec{S}$ decouple in B-field and align to it seperately

Paschen-Back effect: (medium B-field)

We now add spin-orbit coupling $\hat{H}' = \hat{H}_c = \xi(r)\, \hat{L}\cdot\vec{S}$ as a perturbation.

This is for slightly lower fields

Can use non-degenerate PT (see book for subtle reasons) (Eq. (1.26)) to find

$$\Delta E = \langle \phi_{nlm_s} | \hat{H}' | \phi_{nlm_s} \rangle$$

$$= \langle \phi_{nlm_s} | \xi(r)(\hat{L}_x \hat{S}_x + \hat{L}_y \hat{S}_y + \hat{L}_z \hat{S}_z) | \phi_{nlm_s} \rangle$$

Use raising & lowering ~~operators~~ (book 2.185)

$$\hat{L}_\pm = \hat{L}_x \pm i \hat{L}_y \Rightarrow \hat{L}_x = (\hat{L}_+ + \hat{L}_-)/2$$

$$\hat{L}_y = -i(\hat{L}_+ - \hat{L}_-)/2 \quad (2.19)$$

~~$\hat{L}_\pm Y_{lm}(\theta,\phi)$~~

$$\hat{L}_\pm |lm\rangle = \hbar \left[l(l+1) - m(m\pm1) \right]^{\frac{1}{2}} | l (m\pm1) \rangle$$

$$\ldots = \langle \phi_{nlm_s} | \xi(r) \underbrace{\hat{L}_z \hat{S}_z}_{=\hbar^2 m_l \cdot m_s} | \phi_{nlm_s} \rangle = \lambda_{nl}\, m_l \cdot m_s \quad (2.20)$$

with $\lambda_{nl} = \hbar^2 \int_0^\infty dr\, r^2 \left[R_{nl}(r) \right]^2 \xi(r) = -\frac{\alpha^2 Z^2}{n} E_n \frac{1}{\left[l(l+\frac{1}{2})(l+1) \right]}$ $\quad l \neq 0$

- Now shift dependent on l (unlike (2.18))

Anomalous Zeeman effect: (weak B-field, most common case)

historical

$$\hat{H}_0 = \hat{H}_a + \hat{H}_b + \hat{H}_c \qquad \hat{H}' = \hat{H}_d \qquad \left(\text{still neglect } \hat{H}_e\right)$$

Eigenstates of $\hat{H}_0$ same as for finestructure (section 2.1.2)

$$|\phi_{njlm_j}\rangle = \cancel{\sum \langle \phi_{nlm_l} s m_s | \phi_{njlm_j} \rangle \phi_{nlm_l} | s m_s \rangle}$$

Can Expand total angular momentum states in terms of orbital angmom. and spin states

$$| j l m_j \rangle = \sum \underbrace{\langle l m_s m_l m_s | j l m_j \rangle}_{\equiv C_{l s m_l m_s ;\, j l m_j}} | l s m_l m_s \rangle$$

Clebsch-Gordan coefficients: (lots of online calculators available)

$$\Delta E = \left\langle \phi_{n j \ell m_j} \right| \frac{\mu_B}{\hbar}\left(\hat{J}_z + \hat{S}_z\right) B_0 \left| \phi_{n j \ell m_j} \right\rangle$$

$$= \mu_B m_j B_0 + \frac{\mu_B B_0}{\hbar}\left\langle \phi_{n j \ell m_j} \right| \hat{S}_z \left| \phi_{n j \ell m_j} \right\rangle \qquad (2.21)$$

We only look at $s=\frac{1}{2}$ so $j=\ell\pm\frac{1}{2}$.

Then

$$\left|\left(j=\ell+\tfrac{1}{2}\right)\ell\, m_j\right\rangle = \sqrt{\frac{\ell+m_j+\frac{1}{2}}{2\ell+1}}\left|\ell\,\tfrac{1}{2}\; m_\ell=m_j-\tfrac{1}{2}\;\; m_s=\tfrac{1}{2}\right\rangle + \sqrt{\frac{\ell-m_j+\frac{1}{2}}{2\ell+1}}\left|\ell\,\tfrac{1}{2}\; m_\ell=m_j+\tfrac{1}{2}\;\; m_s=-\tfrac{1}{2}\right\rangle$$

↳ check
- $\sum |c_k|^2 = 1$
- $m_j = m_\ell + m_s$

and

$$\left|\left(j=\ell-\tfrac{1}{2}\right)\ell\, m_j\right\rangle = -\sqrt{\frac{\ell-m_j+\frac{1}{2}}{2\ell+1}}\left|\ell\,\tfrac{1}{2}\; m_\ell=m_j-\tfrac{1}{2},\;\; m_s=\tfrac{1}{2}\right\rangle + \sqrt{\frac{\ell+m_j+\frac{1}{2}}{2\ell+1}}\left|\ell\,\tfrac{1}{2}\; m_\ell=m_j+\tfrac{1}{2},\;\; m_s=-\tfrac{1}{2}\right\rangle$$

Insert these into (2.21) & simplify to get anomalous Zeeman shift:

$$\Delta E = g\,\mu_B\, m_j\, B_0 \qquad \text{with Landé g-factor} \qquad g = 1 + \frac{j(j+1)+s(s+1)-\ell(\ell+1)}{2j(j+1)} \qquad (2.22)$$

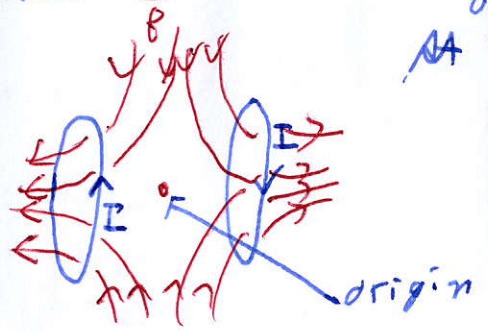
lines = # m_j

- Even stronger fields than for (2.18) ⇒ treat $\hat{H}_e$, even neglect $\hat{H}_B$ ↳ Landau levels
- Even weaker fields than for. (2.22) ⇒ consider Hyperfinestructure (Breit-Rabi-equation) HH

Example for section 2.2 : Magnetic trapping

origin · $\vec{B}=0$

Consider double Helmholtz-coil (quadrupole trap) with current I



Assume a single atom is in $m_j=+\frac{1}{2}$

$$\hookrightarrow \Delta E(\vec{x}) = g\,\mu_B\, m_j \left|\vec{B}(\vec{x})\right| \qquad (2.23)$$

This energy shift increases everywhere away from origin

⇨ atom can be trapped at origin

Q: Can One magnetically trap $m_j<0$ states?

Caution: Typical magnetic traps have so weak fields that we need to look at the Zeeman-effect of hyperfine-structure

Example 2 for section 2.2 (and 2.1) [see online code zeeman_effect_of_finestructure.m]

From strong to weak fields:

- Eq (2.18) and (2.22) predict Energy shifts according to different quantum numbers. What happens in between?

Let us consider Hydrogen $|2p\rangle$. With spin $2p_{\frac{1}{2}}$ $2p_{\frac{3}{2}}$.

Use coupled basis $A = \{ |2p_{\frac{3}{2}}, m_j = \frac{3}{2}\rangle, |\frac{3}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, -\frac{1}{2}\rangle, |\frac{3}{2}, -\frac{3}{2}\rangle, |2p_{\frac{1}{2}}, m_j = -\frac{1}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle \}$

In matrix form

$$\hat{H}_{fs} = \begin{pmatrix} E_{\frac{3}{2}} & & & & & 0 \\ & E_{\frac{3}{2}} & & & & \\ & & E_{\frac{3}{2}} & & & \\ & & & E_{\frac{3}{2}} & & \\ & & & & E_{\frac{1}{2}} & \\ 0 & & & & & E_{\frac{1}{2}} \end{pmatrix}\Bigg|_{\text{Basis } A}$$

fine-structure

From Eq. (2.4)

$$\hat{H}_d = \frac{\mu_B B_0}{\hbar} \begin{array}{c} \hbar(m_e + 2m_s) \\ \begin{pmatrix} \hbar(1+2\cdot\frac{1}{2}) & & & & & \\ & \hbar & & & 0 & \\ & & \cancel{0} & & & \\ & & & 0 & & \\ & 0 & & & \hbar & \\ & & & & & 2\hbar \end{pmatrix} \end{array}$$

Eq (2.17)

Also need uncoupled basis $B = \{ |2p, m_\ell = 1, m_s = \frac{1}{2}\rangle, |0, \frac{1}{2}\rangle, |-1, \frac{1}{2}\rangle, |1, -\frac{1}{2}\rangle, |0, -\frac{1}{2}\rangle, |-1, -\frac{1}{2}\rangle \}$

$$\hat{H}_{TOT} = \hat{H}_{fs} + \hat{U}^{+} \hat{H}_d \hat{U}$$

where $\hat{U}$ is the unitary matrix converting from A to B.

Eigenvalues of $\hat{H}_{TOT}$ as a function of time: